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NEW CHEMICAL IONIZATION REAGENTS DIRECTED TOWARD MASS SPECTROMETRIC ANALYSIS OF TRACE ORGANICS

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Although electron impact ionization is by far the most commonly used ionization technique in analytical mass spectrometry, chemical ionization methods offer unique advantages in many specialized circumstances. Chemical ionization simply makes use of reagent ions generated by ion-molecule reactions in a reagent gas to react with analyte introduced into the CI ion source. For example, the simplest and most frequently used CI technique is CH_4 proton transfer CI in which the ions CH_5^+ and $C_2H_5^+$, generated by reaction of the electron impact produced ions CH_3^+ and CH_4^+ with CH_4 (eqns (1) and (2)) act as super acids in the gas phase toward the analyte, A (eqn(3)).

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2 \quad (1)$$

$$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3 \quad (2)$$

$$CH_5^+(C_2H_5^+) + A \rightarrow AH^+ + CH_4(C_2H_4) \quad (3)$$

Working from a broad base of understanding of the energetics and mechanisms of gas phase ion molecule reactions it is possible to exploit these aspects of the dynamics of reactions to tailor chemical ionization reagents to fill specific needs. For example, in proton transfer CI the amount of energy deposited in the conjugate acid of the analyte will determine the extent of fragmentation (Scheme 1). It is possible to control the amount of energy deposited in AH^+ and

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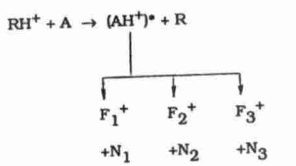

(SCHEME 1)

hence control the extent of fragmentation by using reagent ions derived from compounds R of varying gas phase basicity.

Negative chemical ionization (or ion-molecule reactions involving anions) have received widespread attention recently as a potential means of analysis of compounds of environmental interest, particularly PAH's. However, the use of negative ion EI or CI techniques with chlorinated organics is hampered by the relatively weak C-Cl bond strength and the high electron affinity of chlorine which leads to a considerable degree of dissociative ionization, eqn(4). Thus in such ionization events all information regarding the analyte ACl is lost since the

$$R^- + ACl \rightarrow (R + A) + Cl^- \qquad (4)$$

ionization occurs predominantly as Cl^-. This result can be regarded as being due to the chemical activation of the intermediate ion molecule complex $(RACl^-)^*$ which is sufficient to induce unimolecular decomposition. In order to limit the extent of unimolecular decomposition it is again worthwhile to limit the extent of chemical activation of the $(RACl^-)$ intermediate which can be done by a judicious choice of reagent ion R^-.

Chemical ionization experiments are most frequently performed in relatively gas tight ion sources in conjuction with either magnetic sector or quadrupole mass spectrometric detection. At the pressure employed (~1 torr) with ion residences times of several µsec the average reagent ion will have undergone at least several hundred collisions. Since it is a normal feature of ion molecule reactions that they occur with near unit collision efficiency this means that all or nearly

all of the reagent ion intensity can be converted to analyte ion intensity under appropriate conditions.

All of the experiments done in conjuction with this project were carried out with Fourier Transform Ion Cyclotron Resonance Spectrometry (FTICR). This technique accomplishes chemical ionization at pressures as low as 10^{-9} torr by trapping ions for extremely long periods of time. Most typically in analytical situations pressures of 10^{-6} torr are used with trapping times on the order of 1 sec which allows roughly the same number of collisions to occur as in a conventional CI system. The only differences between the FTICR method and the usual CI system is that at the low pressures of the FTICR termolecular clustering reactions are avoided.

Ethylchloroformate proved to be by far the most promising of the reagents investigated. The sequences of reactions, eqns(5)-(7) readily leads to production of chloride ion adducts. A

$$ClCO_2C_2H_5 \rightarrow Cl- + CO_2C_2H_5 \qquad (5)$$

$$Cl^- + ClCO_2C_2H_5 \rightarrow ClCO_2^- + C_2H_5Cl \qquad (6)$$

$$ClCO_2^- + A \rightarrow ACl^- + CO_2 \qquad (7)$$

competing reaction, eqn(8) potentially leads to a decrease in intensity of ACl^-, however, for most substrates, A, eqn(9), also occurs, leading again to ACl^-. The excellent signal intensities

$$ClCO_2^- + ClCO_2C_2H_5 \rightarrow Cl_2CO_2C_2H_5^- + CO_2 \qquad (8)$$

$$Cl_2CO_2C_2H_5^- + A \rightarrow ACl^- + ClCO_2C_2H_5 \qquad (9)$$

achieved with this reagent system and the facile transfer of Cl^- from CO_2 to a wide variety of compounds led us to investigate extensively the potential of this compound as a Cl^- transfer CI reagent.

This reagent system appears to be applicable to a wide variety of compounds including PAH's and chlorinated aromatics. Representative spectra are shown in **Figure 1.**

The results of FTICR experiments indicate that chloride attachment CI using $ClCO_2C_2H_5$ as a chemical ionization reagent can potentially yield excellent intensities in

quasimolecular ions of a single molecular formula. The method thus has promise in terms of sensitivity for CIMS analysis of compounds ranging from PAH's to dioxins.